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FULL PAPER

Amphiphilic chiral block-poly(thiophene)s: Tuning the blocks.

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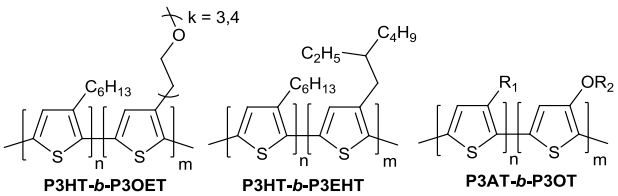
This report describes the synthesis and characterization of amphiphilic block-copoly(3-alkylthiophene)s with one hydrophobic and one hydrophilic block. Implementation of a chiral center in one of the two blocks enables a chiroptical evaluation of the materials in different media. Depending on the solvent conditions, phase-separation and selective aggregation of one of both blocks becomes feasible, which has implications on the aggregation behavior of the second block. The presented chiroptical and thermal study provides an insight into the self-assembly of these materials both in solution and in film.

Introduction

The unusual optical and electronic behavior of conjugated polymers (CPs) makes them very valuable materials for exceptional applications today and in the future. This is shown already by their use in organic solar cells, organic LED's, supercapacitors, biosensors, *etc*.[1] A decisive step forward in the research on CPs was the possibility to perform a controlled polymerization mechanism, initiated by the research groups of McCullough and Yokozawa on poly(thiophene) with Ni(dppp)Cl_2 as a catalyst in 2004.[2–5] Thanks of this, it became possible to have control over the molar mass, regioregularity and molecular topology (block-copolymers, star-shaped polymers, *etc*). Furthermore, a multiplicity of tailor-made homopolymers and random copolymers with a predetermined functionalization became accessible. Current challenge holds the synthesis of functionalized and predetermined block-copolymers in a controlled fashion, combining two different blocks to create more advanced materials with exceptional morphologies. This paves the path towards a full understanding of the structure-property relationships.

All-conjugated block-copolymers can be realized in two ways: either two different monomers are employed[6–22] or the same type of monomer but with different side chains is used[23–42]. Depending on the choice of the side chains, the latter approach can result in significantly different behavior of each block. Block-copoly(thiophene)s composed of blocks with different solubility have already been synthesized before and their aggregation has been studied. Poly(3-hexylthiophene)-*b*-poly(3-(oligoether)thiophene) (**P3HT-*b*-P3OET** – see Scheme 1) has been synthesized at numerous occasions and is defined as a rod-rod block-copolymer.[29–34] These copolymers organize themselves in highly ordered structures, such as lamellae, micelles and vesicles, depending on the ratio of the blocks, the presence of metal ions and the rate of the self-assembly process when exposed to methanol.[31–33] The block

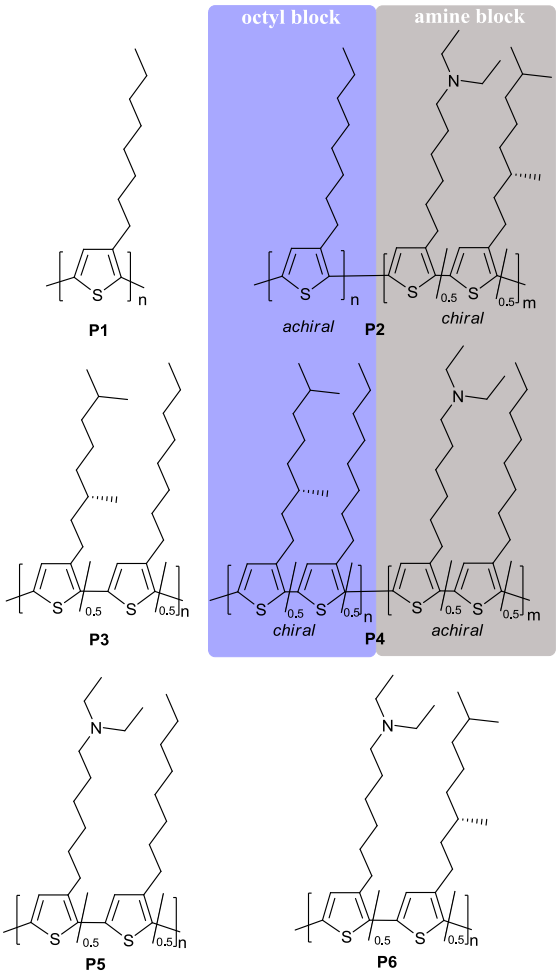


Scheme 1: Examples of block-copolymers synthesized in the past (R = an alkyl group).

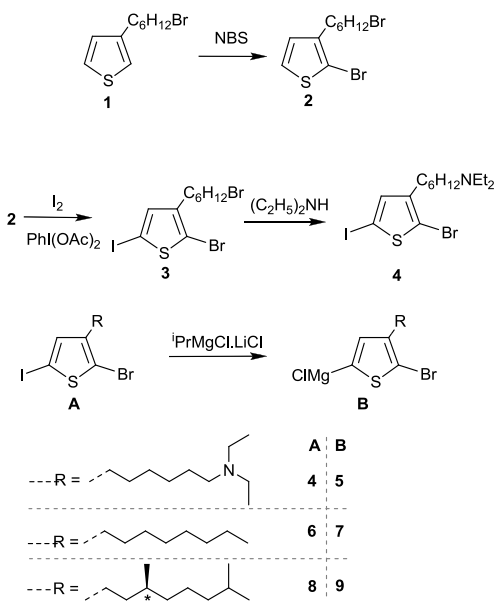
with the hydrophobic hexyl side chains π-stacks and is shielded from the solvent, while the hydrophilic block interacts with methanol. Also poly(3-hexylthiophene)-*b*-poly(3-(2-ethylhexyl)-thiophene)s (**P3HT-*b*-P3EHT** – see Scheme 1) are well-studied block-copolymers that show microphase separation and increased crystallinity compared to P3HT.[34,37] The latter property makes this polymer very promising for application in organic solar cells.[35,36] Further on, block-copolymers with differences in length of the side chain have also been synthesized.[40–42] Jing *et al.* revealed that a difference in side chain length of at least two carbon atoms is needed to induce phase separation during aggregation.[41]

The introduction of a chiral center in the polymers allows investigation of the aggregation behavior by circular dichroism spectroscopy (CD). Block-copolymers of the same overall chain length but with different fractions of the chiral block showed that there is no (linear) relationship between the chiral expression and the chiral content.[42] Studies of block-copolymers of poly(thiophene) with alkyl and alkoxy pendants (**P3AT-*b*-P3OT** – see Scheme 1) have also been investigated.[38,39] The less soluble **P3OT** block aggregates first and imposes its chirality or achirality on the aggregating **P3AT** block while further decreasing the solvent quality.

The difference in solubility of both blocks in all the block-copolymers given above at certain nonsolvent concentrations is significant but small and not tuneable. Indeed, there is no way to tune the solubility of one of both blocks and the order of



Scheme 2: The amphiphilic block-copolymers **P2** and **P4**, the homopolymer **P1** and the random copolymers **P3**, **P5** and **P6**.



Scheme 3: Synthesis of the precursor monomer **4** and monomers **5**, **7** and **9**.

aggregation is predefined from the start. This manuscript describes the synthesis of block-copolymers with a tuneable pronounced difference in solubility between both blocks. The molecular design comprises one hydrophobic poly(3-octylthiophene) block and one poly(3-(6-diethylamino)hexylthiophene) block (**P2** and **P4** - Scheme 2). Due to the implementation of the amine-function in one of both blocks, we can easily change this block from being hydrophobic to hydrophilic by adding acid and the reverse is possible by adding base. To allow the chiroptical evaluation of the polymer aggregation in different solutions, chirality is introduced by means of a 3-((*S*)-3,7-dimethyloctyl)thiophene monomer. Since previous studies have shown that already a very high chiral response is present when only 50% chiral monomers are incorporated,[42] the latter is introduced as a 50% random-copolymer in the block that is aimed to be chiral. To maintain the functional group balance in the different block-copolymers, the achiral block is designed as a random-copolymer with 50 % of 3-octylthiophene. Besides poly(3-octylthiophene)-*b*-poly((*S*)-3,7-dimethyloctylthiophene-*co*-3-[6-(diethylamino)hexyl]thiophene) (**P2**) and poly(3-octylthiophene-*co*-(*S*)-3,7-dimethyloctylthiophene)-*b*-poly(3-octylthiophene-*co*-3-[6-(diethylamino)hexyl]thiophene) (**P4**), we also synthesized the different blocks separately as a reference, in particular random-copolymers **P5** and **P6** (Scheme 2). For the synthesis and chiroptical evaluation of **P1** and **P3** the reader is referred to previous research by our group.[42]

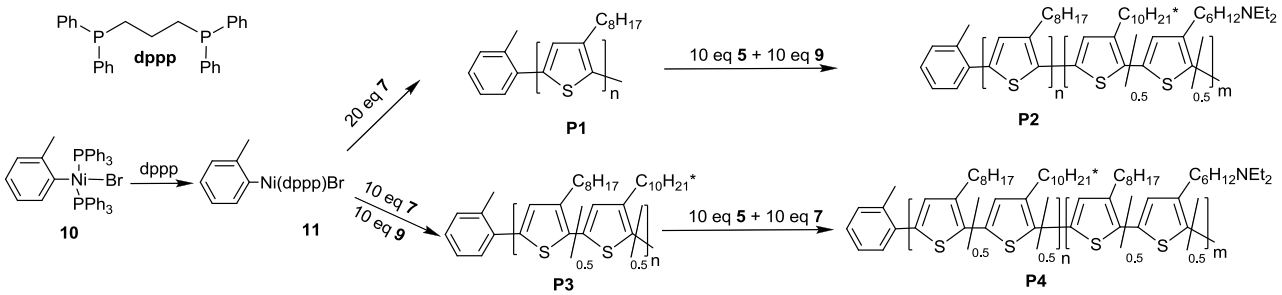
Results and discussion

Monomer synthesis.

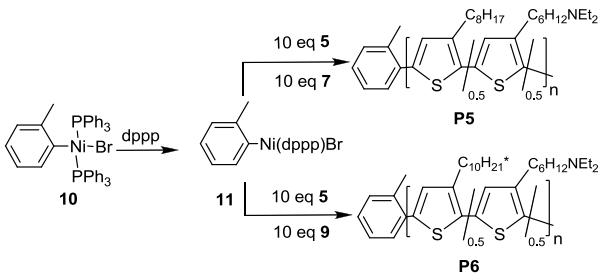
The synthesis of 2-bromo-5-iodo-3-octylthiophene (**6**) and 2-bromo-5-iodo-3-(*S*)-3,7-dimethyloctylthiophene (**8**) was performed as described before.[38,43] The synthesis of 2-bromo-5-iodo-3-[6-(diethylamino)hexyl]thiophene (**4**) is shown in Scheme 3, starting from **1**.[44] Bromination on the 2-position of **1** with *N*-bromosuccinimide (NBS) resulted in compound **2**, after which iodination with I_2 and iodobenzene diacetate led to **3**. Conversion of the bromoalkyl to an amine function with diethyl amine gave the amphiphilic precursor monomer **4**. All the precursor monomers **4**, **6** and **8** were converted to the corresponding monomers **5**, **7** and **9**, respectively, by treatment with ^{i}PrMgCl.LiCl.

Polymer synthesis.

The block-copolymers were synthesized using a Kumada cross-coupling reaction with nickel(1,3-bis(diphenylphosphino)propane) (Ni(dppp)) as a catalyst moiety. The initiator **11** was prepared starting from bromo(*o*-tolyl)bis(triphenylphosphine)nickel(II) (**10**) and dppp (see Scheme 4).[43] This initiator guarantees unidirectional growth of the block-copolymers instead of the bidirectional growth observed for Ni(dppp)Cl_2.[42,45] The monomers required for the first block were mixed in a 1/1 ratio, added to this initiator and polymerized for one hour. In a subsequent step, the monomers of the second block were combined in equimolar amounts and cannulated to the polymerization vessel. The monomer/initiator ratio was defined to obtain diblock-copolymers with a degree of polymerization of 40, corresponding to 20 monomers per block.



Scheme 4: Synthesis of the block-copolymers **P2** and **P4** starting from precursor initiator **10**.



Scheme 5: Synthesis of the random-copolymers **P5** and **P6.**

Table 1 $\overline{M_n}$, $\overline{M_w}$, PDI and degrees of polymerization (DP) values of the synthesized block-copolymers and random-copolymers.

Polymer	$\overline{M_n}$ (kg/mol)	$\overline{M_w}$(kg/mol)	PDI	DP[a]
P2	14.0	15.6	1.1	Octyl block: 28 Amine block: 23
P4	14.6	16.6	1.1	Octyl block: 27 Amine block: 27
P5	10.3	14.8	1.4	37
P6	5.5	6.3	1.1	18

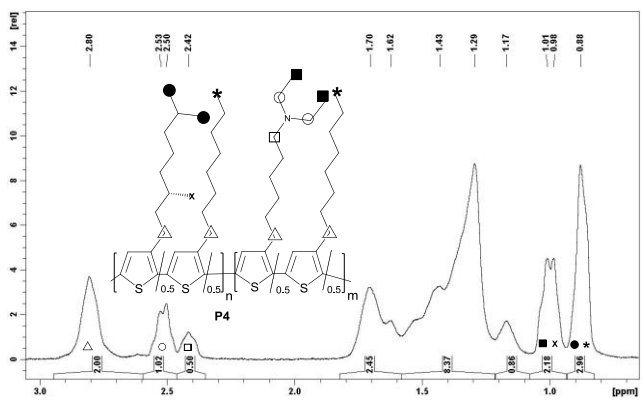


Fig. 1 ^{1}H NMR spectrum of **P4** in $CDCl_3$ with assignment of the peaks used to calculate the proportions of the different monomers.

Table 2 Theoretical and ^{1}H-NMR derived amounts of the different monomers in the synthesized block-copolymers.

	Feed			Experimental		
	5 (%)	**7** (%)	**9** (%)	**5** (%)	**7** (%)	**9** (%)
P2	25	50	25	25	54	21
P4	25	50	25	24	52	24
P5	50	50	/	41	59	/
P6	50	/	50	46	/	54

The polymerization was terminated two hours after the second monomer addition by adding acidified THF. The above strategy exploits the living chain-growth nature of the polymerization to obtain controlled block-copolymers with fixed length of both blocks (see Scheme 4 and Scheme 5).

Polymer characteristics

The synthesized polymers were subjected to size exclusion chromatography in a 5 vol% triethylamine-THF solution toward polystyrene standards. The results are listed in Table 1.

The observed molar masses for the block-copolymers correspond to a degree of polymerization of ~65 which is, taking into account the overestimation of a poly(thiophene) by a factor 1.3 in GPC calibrated with poly(styrene) standards,[46] in good agreement with the predetermined value of 40 monomer units. More importantly, both block-copolymers **P2** and **P4** have nearly the same molar mass, which allows them to be compared directly in chiroptical evaluation.

The ^{1}H NMR spectra allow the structural determination of the polymers. The polymers are intended to be regioregular, with random distribution of the monomer in each block. The former is confirmed by ^{1}H NMR spectroscopy (see ESI). Next, the integration of the α-methylene protons at 2.80 ppm and the integration of the triplet of the protons on the 6-position of the side chain in the amine-monomer at 2.41 ppm allows to calculate the amine-monomer content in the polymer (see Fig. 1 and Table 2). As aimed, approximately one quarter of each block-copolymers **P2** and **P4** is an amine-monomer. The random-copolymers **P5** and **P6** contain 41% and 46% amine monomers respectively. Both signals around 1.00 ppm and 0.88 ppm correspond to the terminal methyl groups in the side chains of the monomers. The signal at 1.00 ppm contains the two methyl groups of the diethyl tails on the amine-monomer (6 H) and the methyl group on the chiral carbon atom of the chiral monomer (3 H). The signal at 0.88 ppm is related to the two terminal methyl

groups on the 7-position in the side chain of the chiral monomer (6 H) and the terminal methyl group of the achiral monomer pendant (3 H). These integrations, together with the ratio of amine content determined above, allow to define the ratio of monomers with an *n*-octyl chain and a chiral octyl chain in **P2** and **P4** (see Table 2). There is a clear correspondence between the aimed block-copolymer structure and the experimental values.

Chiroptical properties of P2, P4, P5 and P6 in solution

To investigate the aggregation behavior of the polymer chains under neutral and acidified conditions, a solvatochromism experiment was performed by gradually increasing the methanol concentrations in THF. Methanol is a nonsolvent for the neutral polymers, whereas THF can be considered as a good solvent. The resulting UV-vis spectra and CD spectra were evaluated to rule out whether the blocks aggregate together or separately, and – if the latter is the case – to determine which block is aggregating first and how this influences the second block. Both block-copolymers **P2** and **P4** and random-copolymers **P3, P5** and **P6** were subjected to these solvatochromism experiments. All UV-vis and CD spectra are given in the Electronic Supplementary Information. In order to evaluate and compare the chiral responses of the reported polymers, the g_{abs} values were calculated *via* Equation 1:

$$g_{abs} = \frac{\Delta\varepsilon}{\varepsilon} = \frac{2(A_L - A_R)}{A_L + A_R} \qquad \textbf{(eq. 1)}$$

with A_L and A_R the absorption of the left- and right-handed circularly polarized light, respectively.

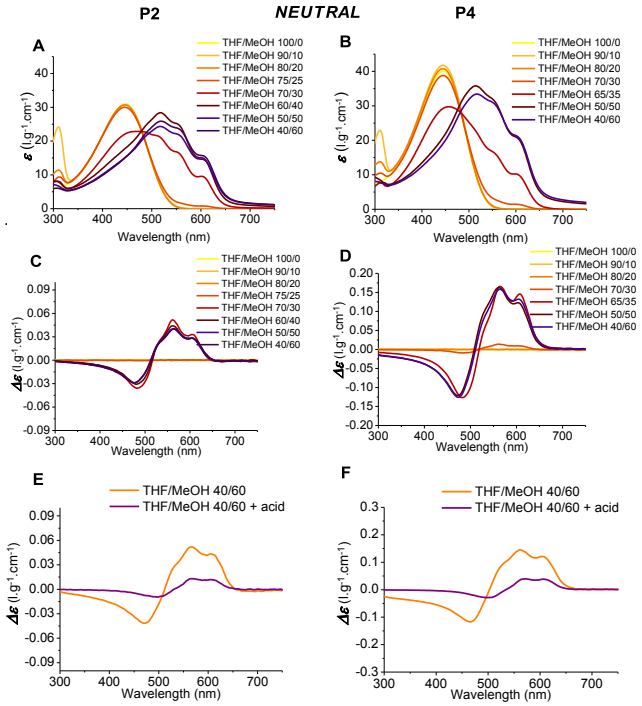


Fig. 2 UV-vis (A,B) and CD spectra (C,D) during solvatochromism experiments for polymers **P2** (A,C) and **P4** (B,D) in neutral solutions. E and F show the influence of adding acid to the neutral THF/MeOH 4/6 solutions on the CD spectra of **P2** and **P4**, respectively.

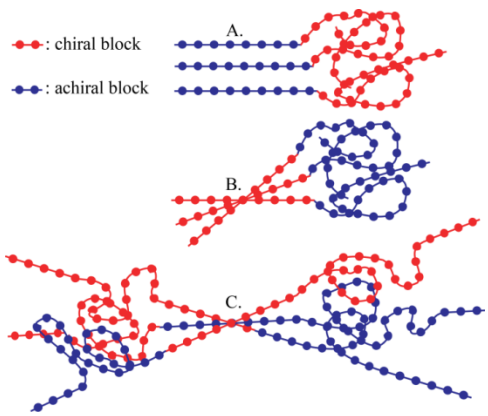


Fig. 3 Proposed models for the aggregation process of block-copolymers **P2** and **P4** when dissolved in a neutral environment during increase of the methanol content. (A) The chiral block is still dissolved and the achiral one is aggregated, (B) the achiral block is still dissolved while the chiral block is aggregated or (C) the entire block-copolymer is in an on-going aggregation transition with each block partly aggregated and partly dissolved. (Courtesy of Julie Pittevils.)

Neutral media - The polymers were dissolved in THF (**P2** and **P5** = 0.021 g L^{-1}; **P4** and **P6** = 0.022 g L^{-1}) and a 1.12 mM NaOH-solution in methanol was added gradually. The basified methanol ensures that the amine functions in the side chains are not protonated and therefore uncharged. The UV-vis spectra in Fig. 2 reveal that **P2** and **P4** start to aggregate at 30 vol% and 35 vol% methanol content, respectively. Since the spectra at these nonsolvent concentrations show the characteristic absorptions of (i) dissolved polymer chains at 450 nm and (ii) aggregated polymer chains at wavelengths between 500 nm and 650 nm, we can conclude that a part of the polymer is still in the dissolved coil conformation and a part has already aggregated. Therefore, three possibilities arise (see Fig. 3): (A) either the chiral block is still dissolved and the achiral one is aggregated; (B) the achiral block is still dissolved while the chiral block is aggregated; or (C) the entire block-copolymer is in an on-going aggregation transition with each block partly aggregated and partly dissolved. Since the CD spectra of both block-copolymers in Fig. 2 already show a CD signal at the nonsolvent concentrations given above, we can rule out the first possibility and two possibilities remain: either the chiral block aggregates first and will impose its chiral stacking upon the achiral block when it aggregates, or both blocks aggregate simultaneously and form mixed aggregates. The maximum g_{abs} values for **P2** and **P4** (3.75×10^{-3} and 7.5×10^{-3}, respectively) correspond to the values measured for the random-copolymer of the chiral block in each of the two block-copolymers, *i.e.* **P6** for **P2** and **P3** for **P4** (see SI – Fig. S13 and S18). The difference between the g_{abs} values of **P2** and **P4** is probably caused by the more pronounced steric hindrance due to the more bulky side chain of the amine-monomer: since in **P2** the chiral entities are distributed between these more bulky side chains compared to the achiral pendants, a less effective chiral expression occurs for this polymer.

At a methanol concentration of 60 vol%, two droplets of acid (concentrated HCl,12 M) were added to the polymer solution. This charges the amine-containing blocks in the block-copolymers. Both block-copolymers show a (nearly) complete

disappearance of the CD signals after adding the acid (see Fig. 2). This lets us conclude that the whole chiral aggregates are disrupted because of the positive charge in the chains. This rules out the possibility of phase-separation between the amine block

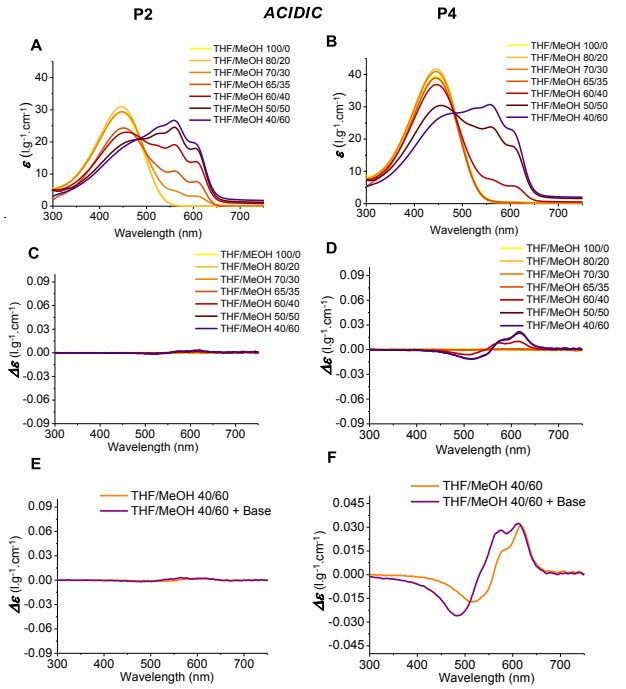


Fig. 4 UV-vis (A,B) and CD spectra (C,D) during solvatochromism experiments for polymers **P2** (A,C) and **P4** (B,D) in acidic solutions. E and F show the influence of adding base to the acidic THF/MeOH 4/6 solutions on the CD spectra of **P2** and **P4,** respectively.

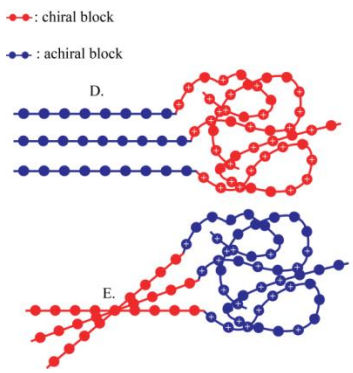


Fig. 5 Proposed models for the aggregation process of block-copolymers **P2** and **P4** when dissolved in an acidic environment during increase of the methanol content. (D) For the case in which the chiral entity is implemented in the charged amine block (**P2**). (E) For the case in which the chiral entity is implemented in the uncharged octyl block (**P4**). (Courtesy of Julie Pittevils.)

and the other block. If this would have been the case, the non-amine block would remain chirally aggregated after addition of acid, and more or less half of the CD effect would remain. We can thus conclude that no phase separation takes place during the aggregation of both block-copolymers and that possibility (C), *i.e.* the simultaneous aggregation of both blocks and the formation of mixed aggregates, remains (see Fig. 3).

In conclusion, in neutral media the block-copolymers act like chiral 3-alkylthiophene copolymers without any phase separation and the chiral monomer forces the achiral monomers to aggregate in a chiral way. Depending on the bulkiness of the comonomer polymerized with the chiral monomer, chirality is more or less expressed. Charging of the amine-functions disrupts the aggregates completely and the CD signals disappear.

Acidic media – The solvatochromism experiments were repeated in acidified media. The block-copolymers were dissolved in a 1.12 mM HCl-solution in THF (**P2** and **P5** = 0.021 g L^{-1}; **P4** and **P6** = 0.022 g L^{-1}) and methanol was added gradually. After each methanol addition, UV-vis and CD spectra were recorded (see Fig. 4). Since the amine functions are now protonated by the acid right from the start, the block-copolymers are amphiphilic and the amine-containing block is soluble in methanol. Indeed, at 60 vol% methanol content in THF, a concentration at which the polymers are already completely aggregated in neutral media, the absorption bands at 450 nm (corresponding to dissolved polymer coils) and between 500 nm and 650 nm (corresponding to aggregated polymer chains) are still both present. Thus, a part of the polymer chain is aggregated, while another part is still dissolved.

For **P2**, the CD spectrum (see Fig. 4) does not reveal any Cotton effects which means that the stacked chains are aggregated in an achiral way. This is in line with an achirally stacked octyl block and a chiral hydrophilic amine block that is not aggregated (see Fig. 5). A solvatochromism experiment (both UV-vis and CD spectroscopy) on random-copolymer **P6**, *i.e.* the chiral block of **P2**, confirms that there is no aggregation of this block at 60 vol% methanol in an acidic medium (see ESI – Fig. S26). Adding some droplets of a concentrated solution of base in methanol (NaOH, 1 M) to the mixture of polymer and THF/methanol 60/40 deprotonates the ammonium groups and results in aggregation of the amine block. This is observed in UV-vis spectroscopy as a disappearance of the absorption band at 450 nm (see ESI – Fig. S21). Since the achiral part was already aggregated, it forces the (chiral) amine block to stack in an achiral way as well and no Cotton effect is observed in CD spectroscopy (see Fig. 4), despite the presence of chiral entities. This behavior has also been observed before in block-copolymers with alkyl and alkoxy side chains and was referred to as "first come, first served".[39]

Evaluation of the CD spectrum of **P4** (see Fig. 4) reveals a small but clear CD signal starting from 40 vol% methanol concentration. Since the chiral building block is present in the neutral block and not in the dissolved hydrophilic block, the aggregation of the chiral neutral block allows chiral expression (see Fig. 5) with g_{abs} values of 2×10^{-3}. Addition of a concentrated NaOH-solution in methanol (1 M) at a 60 vol% methanol content again deprotonates the amine functions and results in aggregation of the amine block. Doing this results in the vanishing of the absorption band at 450 nm in UV-vis spectroscopy and an increase of the Cotton effects in CD spectroscopy (see Fig. 4), and is accompanied by an increase in the g_{abs} value from 2×10^{-3} to 3×10^{-2}. The latter observation is the result of an increased amount of chirally stacked polymer chains: the (achiral) amine block is forced to stack in a chiral way by the first stacked chiral block.

In conclusion, the amphiphilic amine block of block-copolymers **P2** and **P4** is protonated in acidic media and remains dissolved at high methanol concentration. The remaining neutral block

aggregates in such media in a chiral or achiral way, depending on the position of the chiral entities (*i.e.* in or not in the amine block). Adding base to the polymer solutions leads to stacking of the amine blocks in a way determined by the block that has aggregated first (*i.e.* the non-amine octyl block).

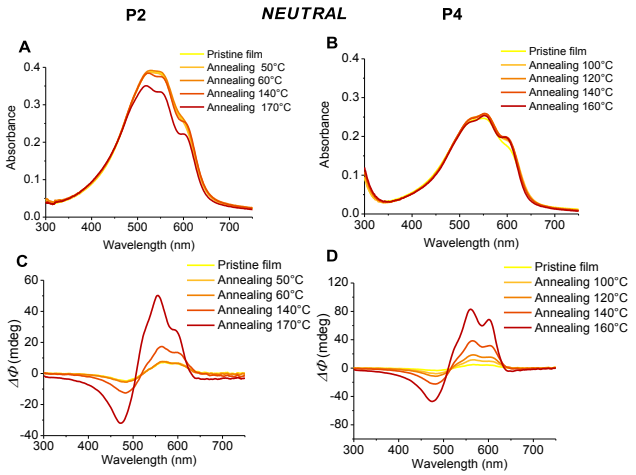


Fig. 6 UV-vis spectra (A,B) and CD spectra (C,D) of films of polymers **P2** (A,C) and **P4** (B,D) spincoated from a neutral THF solution.

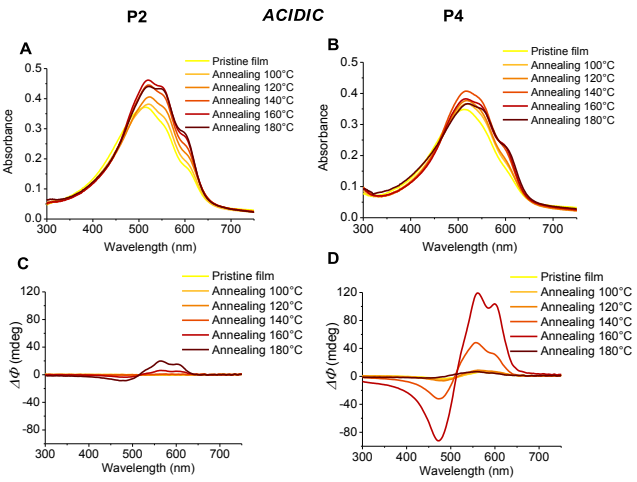


Fig. 7 UV-vis spectra (A,B) and CD spectra (C,D) of films of polymers **P2** (A,C) and **P4** (B,D) spincoated from an acidic THF solution.

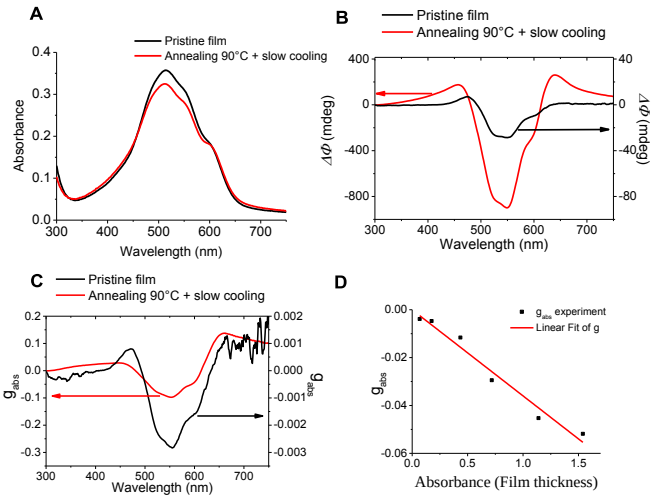


Fig. 8 UV-vis spectra (A), CD spectra (B) and g_{abs} spectra (C) of films of **P6** spincoated from a neutral THF solution, before and after annealing for 1 minute at 90 °C subsequent cooling to 50 °C at 2 °C min.$^{-1}$. (D) Correlation between g_{abs} and the film thickness.

Chiroptical properties of P2, P4 and P5 in film

The polymers **P2**, **P4** and **P5** were dissolved in neutral or acidified THF (10 mg mL^{-1}) and spincoated on glass substrates. The chiroptical properties of the films were evaluated with UV-vis and CD spectroscopy.

Neutral media – The as prepared films of the block-copolymers **P2** and **P4**, spincoated from the neutral THF solutions, show only small Cotton effects and g_{abs} values near ~ 10^{-3} (see ESI - Fig. S28 and S31). Subsequently the films were annealed at 170 °C (**P2**) or 160 °C (**P4**) during one minute and then quickly brought to room temperature by fast cooling. These annealing temperatures were derived from the DSC experiments (*vide infra*) and are located in the region of the melting temperature. The increased mobility of heated polymer chains allows them to re-organize in a more optimal chiral organization, resulting in increased g_{abs} values (see Fig. 6). Since the amine block is not protonated, the block-copolymers act like chiral poly(3-alkylthiophene)s without any phase separation. Maximum g_{abs} values for **P2** and **P4** are 5×10^{-3} and 1×10^{-2}, respectively. Again, as in the solutions of the aggregated polymers, the higher g_{abs} value of **P4** can be related to the better chiral stacking that can be achieved when the chiral entity is in the less sterically demanding non-amine block. Slow cooling (2 °C min^{-1}) does not result in higher g_{abs} values of **P2** or **P4**. Nevertheless, **P4** shows an inversion of the bisignate Cotton effect after heating at 160 °C and slow cooling to 50 °C (2 °C min^{-1}) (see ESI – Fig. S32), as previously shown for other chiral poly(thiophene)s by the group of Meijer.[47]

Acidic media – Films were also spincoated from THF solutions enriched with a droplet of concentrated HCl resulting in positively charged amine blocks of the block-copolymers. The CD spectrum of the as-prepared film of **P2** does not show any Cotton effects. Since the chiral entity is present in the disordered, charged amine block, the chirality cannot be expressed. Annealing for one minute at 140 °C and fast cooling does not result in any changes. However, annealing at 170 °C or

160 °C does afford Cotton effects (see Fig. 7). Presumably, these effects result from the evaporation of HCl at these elevated temperatures which causes deprotonation of the ammonium functions in the chiral block and the subsequent organisation in a chiral manner. For **P4**, a very small Cotton effect is observed in the freshly spincoated films. The same phenomena as seen for **P2** at 160 °C and 180 °C are observed.

The random-copolymer **P5** does not afford any CD signals nor in neutral nor in acidic media, even after annealing at 90 °C.

Chiroptical properties of P6 in film

During the annealing experiments described above, the random-copolymer **P6** (which can be considered to be the chiral analogue of **P5**) showed a peculiar behavior in CD spectroscopy, which was not observed for the other considered copolymers. A very high ellipticity ($\phi > 2$ degrees) and a very high value of g_{abs} up to 0.14 is observed when annealing the film for one minute at 90 °C followed by slow cooling (2 °C min^{-1}) to 25 °C (see Fig. 8 A-C). Moreover, this phenomenon is not observed when cooling fast, *i.e.* direct exposure to room temperature after annealing. The high values are not influenced when CD spectra are collected under different angles. This observation has also been reported in the past by other research groups for poly(fluorene)s,[48–53] poly(*p*-phenyleneethynylene)s[54–57] and a few poly(thiophene)s.[58–61] The highest values for g_{abs} belong to the poly(fluorene)s ($g_{abs} \sim 0.25$) and the poly(*p*-phenyleneethynylene)s ($g_{abs} \sim 0.37$). For poly(thiophene)s, typical g_{abs} values for absorption are around 0.02, but values as high as 0.08 have already been reported.[58] To the best of our knowledge, we are the first to report g_{abs} values of 0.14 for poly(thiophene)s.

In fact, the CD spectra obtained for **P6** films are a superposition of two distinct effects. On the one hand true circular dichroism occurs which results in a bisignate Cotton-effect in CD spectroscopy caused by the Davydov-splitting.[62] The g_{abs} values correlated with this effect are in the order of $\leq 10^{-2}$ and are obtained for a pristine **P6** film. On the other hand a pseudo circular dichroism effect is also present.[53] The latter does not originate from chiral aggregates formed during annealing of the polymer film itself, but from a more extended long-range order present in the chiral polymer aggregates. Indeed, the polymers shows thermotropic liquid crystalline properties; annealing a **P6** film in its mesophase temperature range (during slow cooling from 90 °C) allows efficient supramolecular ordening of the molecules in the film, which is responsible for the pseudo-circular dichroism. The mesomorphic properties were confirmed by investigating thin films of **P6** (on microscopy glass slides rinsed with chloroform and aceton and spincoated from solutions in neutral THF) by means of polarizing optical microscopy (POM). At 90 °C, the material is in its isotropic liquid state, and no texture can be observed between crossed polarizers. However, on slow cooling below about 85 °C a birefringent Schlieren-like defect texture appears (see ESI – Fig. S44), but the sample is still flowing and can be sheared. This suggests the formation of a nematic phase – albeit of rather high viscosity. The thermotropic liquid-crystalline properties of **P6** merit further investigation.

'True' chirality is characterized by an absence of correlation between the inherent g_{abs} value and the film thickness, which is not the case for the supramolecular order dependent 'pseudo'-chirality, described by Craig *et al*.[53] Therefore, we evaluated the correlation between the film thickness and the g_{abs} value to validate our assumption of pseudo-chirality. Solutions of **P6** in neutral THF were spincoated on glass substrates under identical conditions starting from different concentrations ranging from 2 to 47 mg mL^{-1} to obtain films of different thickness. All the films were subjected to UV-vis spectroscopy and the height of the peak at 450 nm was taken as a measure of the film thickness. Each of the untreated films only afforded a 'normal' small bisignate CD signal ($g_{abs} = 4 \times 10^{-3}$) for the maximum absolute value. Subsequent annealing followed by the slow cooling process described above leads to enhanced CD signals. It is worthwhile to mention that the thickest film even had an ellipticity of more than 2 degrees, which is out of the range of our equipment and therefore leads to truncation of the spectra. Correlating the corresponding g_{abs} values with the film thickness clearly shows linear dependence (see Fig. 8D), from which we can deduce that the high CD values are originating from pseudo-chirality.

DSC measurements

In order to examine the thermal properties and the crystallization behavior of the reported polymers, DSC measurements were performed on **P1**-**P6.** The polymers were first heated well above their melting temperature, kept at this temperature for 15 minutes and then slowly cooled down at 2°C min^{-1}. Finally, the melting temperatures were also determined by reheating the samples at 10°C min^{-1}. The melting and crystallization temperatures are summarized in Table 3. **P1**, **P3**, **P5** and **P6,** which constitute the respective blocks of block-copolymers **P2** and **P4**, are all semi-crystalline and showed a single melting peak. The melting (T_m) and crystallization (T_{cryst}) temperatures and melting enthalpies decrease with increasing length and branching of the side chain. Indeed, **P1** (only *n*-octyl substituents) shows the highest T_m, while **P6** shows the lowest T_m. Due to the rather narrow mesophase temperature range exhibited by **P6,** its clearing point (*i.e.* the temperature at which the liquid-crystalline phase transforms into the isotropic liquid phase on heating) could not be resolved from the large melting peak in the DSC thermogram; it was determined to be about 85 °C by means of POM. Interestingly, the block-copolymers **P2** and **P4** also show only one melting peak and one crystallization peak, indicating that both blocks co-crystallize. Co-crystallization of block-copoly(3-alkylthiophene)s has already been observed in cases in which the different alkyl side chain differ in only two methylene groups.[41] Clearly, this is also the case in the block-copolymers **P2** and **P4**. It should be noted that the co-crystallization is perfectly in line with the fact that in neutral/basic conditions simultaneous aggregation of both blocks was observed. Obviously, the conditions of both processes are different – in poor solvent upon decreasing the solvent quality *versus* in solid state after cooling down – but it points at the tendency of both blocks to form a supramolecular structure in which both are present without microphase separation.

Table 3 Melting point T_m, crystallization point T_{cryst} and melting enthalpy H° of polymers **P1**-**P6** determined from DSC measurements.

Polymer	T_{cryst} (°C)[a]	T_m (°C)[b]	H° (J/g)[c]
P1	153	181	11.7
P2	154	177	16.1
P3	142	167	17.1
P4	143	168	17.8
P5	118	143	7.2
P6	70	85	6.3

[a] Measured at a cooling rate of 2 °C min^{-1}. [b] Measured during the second heating run at a heating rate of 10 °C min^{-1}. [c] Measured during the second heating run.

Experimental section

Reagents and instrumentation.

All reagents were purchased from Sigma-Aldrich, Acros Organics, Merck and Alfa Aesar. Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). Bromo-(*o*-tolyl)-bis(triphenylphosphine)nickel(II) (**10**),[43] the precursor monomers **6** and **8**,[38] 3-(6-bromohexyl)thiophene (**1**),[44] and the polymers **P1** and **P3**[42] were prepared according to literature procedures. Before each polymerization, a small aliquot of 2-bromo-5-magnesiochloro-3-alkylthiophene was quenched with D_2O and analyzed by ^1H NMR to verify the conversion of the Grignard metathesis reaction. Gel Permeation Chromatography (GPC) measurements were done with a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in THF as eluent toward polystyrene standards. Mass spectra were recorded using an Agilent HP5989. ^1H and ^{13}C nuclear magnetic resonance (^1H and ^{13}C NMR) measurements were carried out with a Bruker Avance 300 MHz, 400 MHz and 600 MHz. UV-vis and CD measurements were performed on a Perkin-Elmer Lambda 900 UV-vis-NIR and a JASCO 62 DS apparatus, respectively. Films for UV-vis and CD experiments were prepared by spin coating (1200 rpm, 20 s) from neutral or acidified THF solutions that were filtered with a Millex hydrophobic fluoropore PTFE filter of 0.20 µm prior to spin coating. DSC measurements were performed with a TA Instruments Q 2000 apparatus. Optical textures were observed with an Olympus BX60 polarizing optical microscope equipped with a Linkam THMS600 heating stage and a Linkam TMS93 programmable temperature controller.

Precursor monomer synthesis

2-Bromo-3-(6-bromohexyl)thiophene (2)

A solution of 3-(6-bromohexyl)thiophene (**1**) (23.8 mmol, 5.89 g) in dry THF (100 mL) is cooled to 0 °C, shielded from light and kept under argon atmosphere. Next, one equivalent of NBS (23.8 mmol, 4.24 g) is added in small portions and the reaction mixture is allowed to reach room temperature. The reaction is monitored with TLC (eluent: heptane) and $NaHS_2O_3$ is added when the reaction is complete. The reaction mixture is extracted with diethylether and washed with a NaOH-solution (2 M), a saturated $NaHCO_3$-solution and brine. Finally, the crude mixture is dried with $MgSO_4$, concentrated under reduced pressure and purified with column chromatography (SiO_2, heptane) to a bright yellow oil (5.48 g, 70%). δ_H (300 MHz; $CDCl_3$): 7.19 (1 H, d, Ar-H), 6.78 (1 H, d, Ar-H), 3.40 (2 H, t, -CH_2-Br), 2.57 (2 H, t, Ar-CH_2-), 1.86 (2 H, m), 1.55 (2 H, m), 1.46 (2 H, m), 1.35 (2 H, m). δ_C (300 MHz, $CDCl_3$): 141.6; 128,3; 125.3; 109.0; 34.1; 32.8; 29.6; 29.3; 28.3; 27.9.

MS (CI): 327 (MH^+)

2-Bromo-5-iodo-3-(6-bromohexyl)thiophene (3)

The brominated compound **2** (1.50 mmol, 0.489 g) is dissolved in CH_2Cl_2 (25 mL), shielded from light and cooled to 0 °C, purged with argon and kept under argon atmosphere. Iodobenzene diacetate (0.6 eq, 0.900 mmol, 0.291 g) and iodine (0.55 eq, 0.830 mmol, 0.209 g) are added to the solution. After 1 h, the reaction mixture is allowed to reach room temperature and is stirred overnight. The conversion is evaluated with ^1H NMR spectroscopy and on completion a $NaHS_2O_3$-solution is added. The mixture is extracted with diethylether and rinsed with a saturated $NaHCO_3$-solution and brine. After drying with $MgSO_4$ and concentration under reduced pressure, the crude mixture is heated under reduced pressure for 3 h to eliminate the remaining iodobenzene. Subsequently, the product is dissolved in heptane and activated coal is added. This mixture is vigorously stirred during 10 min. and then filtered. After concentration under reduced pressure, the product is purified with column chromatography (SiO_2, heptane) to obtain the product (0.480 g, 71%). δ_H (300 MHz; $CDCl_3$): 6.95 (1 H, s, Ar-H), 3.40 (2 H, t, -CH_2-Br), 2.53 (2 H, t, Ar-CH_2-), 1.87 (2 H, m), 1.55 (2 H, m), 1.46 (2 H, m), 1.35 (2 H, m). δ_C (300 MHz, $CDCl_3$): 143.9; 137.9; 111.8; 71.2; 33.9; 32.6; 29.4; 29.0; 28.2; 27.9.

MS (CI): 452 (MH^+)

2-Bromo-5-iodo-3-(6-diethylaminohexyl)thiophene (4)

1.62 g (22.1 mmol) diethylamine is dissolved in acetone (25 mL). A solution of **3** (5.53 mmol, 2.50 g) in acetone (20 mL) is slowly added to the amine solution while stirring. After complete addition, the mixture is heated to 35 °C under reflux during 28 h. Next, a saturated solution of $NaHCO_3$ is added and the crude mixture is extracted with diethylether. Extraction with a HCl-solution (2 M) transfers the product to the aqueous layer. Next, this layer is neutralized with a NaOH-solution and extracted with diethylether. Drying with Na_2SO_4 and evaporation of the solvent under reduced pressure delivers the pure product as a light yellow oil (1.92 g, 82%). δ_H (300 MHz; $CDCl_3$): 6.95 (1 H, s, Ar-H), 2.52 (6 H, m, -CH_2-N-(CH_2-)$_2$), 2.39 (2 H, t, Ar-CH_2-), 1.52 (2 H, m), 1.44 (2 H, m), 1.31 (4 H, m), 1.05 (6 H, t). δ_C (300 MHz, $CDCl_3$): 144.2, 137.9, 111.72, 71.1, 52.9, 46.9, 29.6, 29.1, 29.0, 27.4, 26.8, 11.6.

MS (EI): 444 ($M^{\cdot+}$)

Monomer synthesis

General procedure for the preparation of the monomers.

The precursor monomers **4**, **6** and **8** (4.00 mmol) are dissolved in dry THF (29.09 mL) and purged with argon. *i*-PrMgCl.LiCl (1.37 M in THF; 4.00 mmol, 2.91 mL) is added to the solution, and the reaction is stirred during 45 min. at room temperature under argon atmosphere. The conversion of the GRIM reaction is evaluated by pouring an aliquot of the reaction mixture in D_2O and subsequent analysis in ^1H NMR spectroscopy.

Polymer synthesis

Poly(3-octylthiophene)-*b*-poly((*S*)-3,7-dimethyloctylthiophene-*co*-3-(6-diethylamino)hexylthiophene) (P2)

Compound **10** (50.0 µmol, 37.7 mg) and dppp (0.100 mmol, 41.2 mg) are loaded in a dry flask and dissolved in 2 mL dry THF, purged and kept under argon. This mixture is stirred at room temperature during 30 min. Subsequently, 1.00 mmol (8.00 mL) of the achiral monomer **7** is transferred to the Ni-initiator and allowed to polymerize during 1 h. Meanwhile, 0.500 mmol (4.00 mL) of the chiral monomer **9** and 0.500 mmol (4.00 mL) of the amine monomer **5** are brought together and homogenized. This mixture is transferred to the polymerization mixture and allowed to polymerize for 2 more hours. The polymerization is quenched with a 2 M HCl in THF solution. Next, the polymer is precipitated in slightly basified (NaOH) methanol and washed with acetone using a Soxhlet-extraction. Finally, the polymer is precipitated again in basified methanol, filtered and dried under vacuum. The final polymer is a dark red-brown solid (0.247 g, 58%).

Poly(3-octylthiophene-*co*-(*S*)-3,7-dimethyloctylthiophene)-*b*-poly(3-octylthiophene-*co*-3-(6-diethylamino)hexylthiophene) (P4)

The precursor initiator **10** (50.0 µmol, 37.7 mg) and dppp (0.100 mmol, 41.2 mg) are dissolved in dry THF, purged with argon, stirred during 30 min. and kept under argon atmosphere. Meanwhile, 0.500 mmol (4.00 mL) of the achiral monomer **7** and 0.500 mmol (4.00 mL) of the chiral monomer **9** are brought together and homogenized in a separate flask. When the initiator is stirred for 30 min, the monomer mixture is cannulated to the initiator and the polymerization of the first block is allowed to run for 1 h. Next, 0.500 mmol (4.00 mL) of the achiral monomer **7** and 0.500 mmol (4.00 mL) of the amine monomer **5** are brought together and homogenized and transferred to the polymerization mixture. After 2 h of the last monomer addition, the polymerization is quenched with a 2 M HCl in THF solution. Next, the polymer is precipitated in lightly basified (NaOH) methanol and washed with acetone using a Soxhlet-extraction. Finally, the polymer is precipitated again in basified methanol, filtered and dried under vacuum. The final polymer is a dark red-brown solid (0.149 g, 63%).

Poly(3-octylthiophene-*co*-3-(6-diethylamino)hexylthiophene) (P5)

The initiator is prepared by combining compound **10** (50.0 µmol, 37.7 mg) and dppp (0.100 mmol, 41.2 mg) in dry THF and allowing this mixture to stir for 30 min. at room temperature after purging with argon. In the meantime, 0.500 mmol (4.00 mL) of the achiral monomer **7** and 0.500 mmol (4.00 mL) of the amine monomer **5** are brought together, homogenized, transferred to the polymerization mixture and allowed to polymerize for 2 h. Next, the reaction is stopped by adding a 2 M HCl in THF solution. The polymer is precipitated in methanol which is lightly basified with NaOH. After filtration and a Soxhlet-extraction with acetone, the polymer is precipitated again in basified methanol, filtered and dried under vacuum. The final polymer is a dark red-brown solid (88.9 mg, 41%).

Poly((*S*)-3,7-dimethyloctylthiophene-*co*-3-(6-diethylamino)hexylthiophene) (P6)

A mixture of the Ni-catalyst **10** (50.0 µmmol, 37.7 mg) and dppp (0.100 mmol, 41.2 mg) in dry THF is purged and stirred at room temperature for 30 min. under argon atmosphere. A premixed solution of 0.500 mmol (4.00 mL) of the chiral monomer **9** and 0.500 mmol (4.00 mL) of the amine monomer **5** is transferred to the initiator and the polymerization is allowed to run for 2 h. Subsequently, the polymerization is quenched with 2 M HCl THF solution and precipitated in basified (NaOH) methanol. The polymer is filtered and washed by Soxhlet-extraction with acetone. After precipitation in basified methanol and filtration, the polymer is dried under vacuum and obtained as a dark red-brown solid (34.1 mg, 49%).

Conclusion

We report the successful preparation of amphiphilic block-copoly(thiophene)s in a one-pot synthesis using (*o*-tolyl)-Ni(dppp)Br as an initiator. The use of acids and bases allows us to selectively protonate or deprotonate the amine block whereby this block becomes soluble or insoluble in methanol (a nonsolvent for 'normal' poly(3-alkylthiophene)s), respectively. The chiral center, incorporated in either the hydrophobic block or the hydrophilic block, allowed us to perform a thorough chiroptical study on the polymers in different media both in solution and in film. This revealed the formation of mixed aggregates in a neutral THF solutions during the addition of methanol because of the simultaneous aggregation of both blocks in a neutral medium. This simultaneous aggregation is also reflected in the co-crystallization behavior during the DSC experiments. On the other hand, in an acidic environment only the hydrophobic blocks aggregate and the positively charged amine blocks remain dissolved at high methanol concentrations. As a result, the amine-containing block is forced to adopt the same (chiral or achiral) supramolecular structure as the first block when base is added to deprotonate the amine functions in the side chains. The same behavior is observed in films.

Finally, the random copolymer of a chiral and an amine building block (**P6**) shows a liquid-crystalline behavior resulting in extremely high g_{abs} values correlated to pseudo-chirality.

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Notes and references

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the synthesized polymers, DSC spectra of **P1**-**P6** and a polarizing optical micropscopy texture of the mesomorphic polymer **P6**. See DOI: 10.1039/b000000x/

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TEXTUAL ABSTRACT

Amphiphilic chiral block-copolymers are synthesized and their self-assembly is chiroptically investigated. Co-aggregation and phase separation are observed in neutral and acidic media, respectively.

GRAPHICAL ABSTRACT - TABLE OF CONTENTS